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Equimolar CoNiFeMnCr High Entropy Alloys added with HfC or TaC carbides: possible alternative alloys to superalloys based on the critical Co element and strengthened by HfC or TaC for high temperature applications

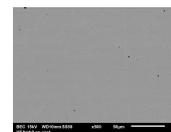
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Cobalt-based superalloys containing carbides and elaborated by conventional casting represent a historically important family of superalloys and can be still considered currently for particular uses such as hot turbine components for aeronautics or power generation, or for glass-forming tools. The ones among these cobalt alloys which are strengthened by MC script-like eutectic carbides located in the intergrains and interdendrites spaces are able to offer very interesting mechanical properties at elevated temperatures. Even if they contain a part of nickel (about 10 wt.%) for stabilizing their austenitic structure at all temperatures [1], and a part of chromium (about 30wt.%) to allow them resisting both hot oxidation by gases and hot corrosion by melts [2], cobalt-based alloys also contain a lot of the critical element Co (50 wt.% and a little more). With the emerging High Entropy Alloys (HEA) which display interesting properties, one can envisage replacing the matrix of these Co-based superalloys by a HEA-type matrix made of more common elements (Fe and Mn notably), to be less dependent on the Co availability.

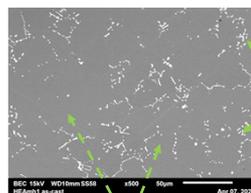
In this work, taking two superalloys with interesting high temperature chemical and mechanical properties as references (Co-25Cr-0.25C-3.7Hf [3] and Co-10Ni-30Cr-0.2C-4Ta [4]), three alloys were elaborated by casting: a well-known equimolar CoNiFeMnCr HEA alloy [5,6] to play the role of reference, and two versions with C and Hf or Ta to promote the formation of HfC or TaC carbides in quantities similar to the two previously cited Co-based superalloys.

As-cast microstructures



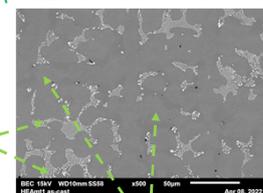
←equimolar CoNiFeMnCr (single-phased, austenitic)

equimolar base + HfC (+0.25 wt.%C +3.7 wt.%Hf)



equimolar CoNiFeMnCr matrix

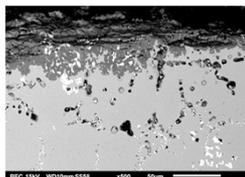
equimolar base + TaC (+0.25 wt.%C +3.7 wt.%Ta)



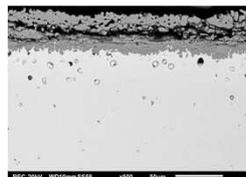
equimolar CoNiFeMnCr matrix containing also 1 to 2 wt.%Ta

High temperature oxidation in laboratory air

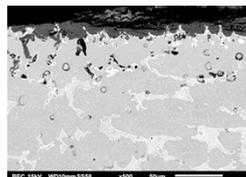
equimolar base + HfC



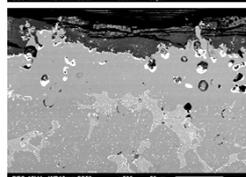
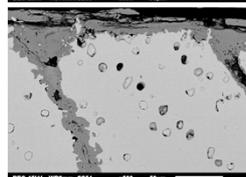
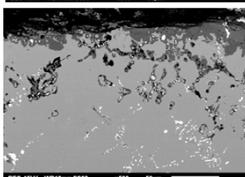
equimolar CoNiFeMnCr



equimolar base + TaC



50h @ 1000°C



50h @ 1100°C

External oxides (and some internal oxides):

clear gray → (Cr, Mn)_yO_x (often the outermost oxides)

medium gray → (Cr, Mn)_xO_y

dark gray → (Cr, Mn)_xO_y, and even chromia (Cr₂O₃) close to the alloy (y/x is close to 2)

Internal oxides (other than the previous ones):

white → HfO₂, pale → CrTaO₄

Chemical changes in the subsurfaces:

Oxidation parameters	Chemical changes	Equimolar + HfC	Equimolar CoNiFeMnCr	Equimolar + TaC
50h @ 1000°C	Wt.%Cr mini	6 – 13 wt.% Cr	8 – 11 wt.% Cr	10 – 11 wt.% Cr
	Cr-depleted depth	50 – 60 µm	50 – 60 µm	50 – 60 µm
	Wt.%Mn mini	2 wt.% Mn	2 – 3 wt.% Mn	2 wt.% Mn
50h @ 1100°C	Mn-depleted depth	100 – 150 µm	60 – 70 µm	> 80 µm
	Wt.%Cr mini	12 wt.% Cr	12 – 12 wt.% Cr	8 – 13 wt.% Cr
	Cr-depleted depth	100 – 130 µm	110 – 120 µm	110 µm
	Wt.%Mn mini	2 – 3 wt.% Mn	2 wt.% Mn	2 wt.% Mn
	Mn-depleted depth	220 – 250 µm	160 – 200 µm	200 µm

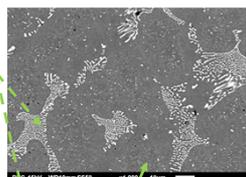
The CoNiFeMnCr equimolar alloy is unsurprisingly single-phased while its versions containing, either Hf and C, or Ta and C, are both double-phased. There are a dendritic matrix composed of the equimolar Hf-free CoNiFeMnCr solution and interdendritic script-like eutectic HfC carbides in the alloy containing additionally Hf and C (and also clusters of compact pre-eutectic HfC). In the alloy containing Ta and C, the matrix is equimolar in Co, Ni, Fe, Mn and Cr but it also contains about 2 wt.%Ta. Its interdendritic carbide network is made of script-like eutectic TaC carbides. Since Hf is – as previously encountered in chromium-rich cobalt [3], nickel [7] and iron [8] based alloys – totally absent in the CoNiFeMnCr matrix, the equimolar alloy added with Hf and C is really the association of the HEA alloy and the HfC carbides (both phases are clearly distinct). This is not really true for the equimolar alloy added with Ta and C since a part of Ta and of C is in the matrix.

At high temperature the primary MC carbides did not morphologically change whatever the exposure temperature, but new carbides precipitated: chromium carbides at 1100°C in the HfC-containing HEA, fine secondary TaC in the matrix of the TaC-containing HEA for both temperatures. These secondary carbides, precipitated from the Ta and C atoms initially present in solid solution in the as-cast alloy's matrix, may be useful to enhance creep resistance. The oxidation behavior was neither good nor catastrophic. However, the significant impoverishment in both Cr and Mn noted after 50 hours at high temperature, let fear an imminent degradation of the behavior of the three alloys. The presence of numerous deep oxidation penetrations in the CoNiFeMnCr alloy only – seemingly intergranular or interdendritic – evidences a possible beneficial influence of the presence of the carbides. Anyway, the oxidation behavior must be improved, by increasing the Cr content for instance. No data concerning the creep behavior are available today. However first creep tests are scheduled for the next weeks.

In case of good resistances against hot oxidation (and corrosion) and against creep deformation, these MC-containing HEA may be alternative to [Co,Ni]-based superalloys.

Bulk microstructure evolution at high temperature

50h @ 1000°C

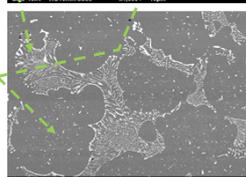


eutectic TaC not affected by the H.T. exposures

eutectic and pre-eutectic HfC not affected by the H.T. exposures

precipitation of coarse chromium carbides (Cr₇C₃)

50h @ 1100°C



secondary TaC precipitated during the H.T. exposures

